
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: WU et al.

Attorney Docket No.:

NOVLP098/NVLS-2907

Application No.: 10/800,409

Examiner: CHEN, Brett

Filed: March 11, 2004

Group: 1762

Title: METHODS FOR PRODUCING LOW-K
CDO FILMS

Confirmation No.: 7038

DECLARATION UNDER 37 CFR § 1.132

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

I, Qingguo Wu declare as follows:


1. I joined Novellus Systems, Inc., assignee of the above-identified patent application, as a scientist in 2002. Prior to joining Novellus, I worked in the Department of Chemical Engineering at the Massachusetts Institute of Technology as a postdoctoral associate for 2 years. I received a Ph.D. from Queen's University, Canada in 2000 and a M.S. from Henan University, China in 1990. I was a visiting scientist and worked in the Department of Chemistry at Cornell University before joining Professor Suning Wang's group at Queen's University in 1997. I have authored or coauthored more than 50 publications in refereed journals and am an inventor on 4 patents and 9 patent applications. My research efforts include the research and development of low-k dielectrics and low-k barrier materials. I also research film process optimization to address the integration and reliability issues in early development stage.
2. I have extensive experience in depositing and evaluating carbon doped oxide films. At Novellus, I have over the past few years been involved with or directed the deposition of hundreds of carbon doped oxide films. I have evaluated the chemical and mechanical properties of these films according to standard protocols employed in the field.

3. I am an inventor of the subject matter described and claimed in the above-identified patent application. The patent application describes and claims methods of depositing carbon-doped oxide films having low stress and dielectric constant by using a primary organosilicon CDO precursor and a secondary carbon-carbon triple bond containing organosilicon CDO precursor.
4. We found in our work that using a primary CDO precursor + carbon-carbon triple bond containing secondary CDO precursor are critical in obtaining low dielectric constant and low stress. Our work shows the unexpected result that primary CDO precursor + carbon-carbon triple bond-containing organosilicon secondary CDO precursor provide improvements in stress and k that saturated CDO precursor and unsaturated hydrocarbon compound does not.
5. Attached in Appendix B is a direct comparison of primary CDO precursor + C≡C-containing organosilicon secondary CDO precursor with saturated CDO precursor + unsaturated hydrocarbon compound. Figure 1 shows dielectric constant and stress as a function of unsaturated CDO precursor flow rate using DEMS as a primary precursor and ETMS (TMSA) as a secondary precursor. Both dielectric constant and film stress decrease with increasing secondary CDO precursor (ETMS). Figure 2 shows dielectric constant and stress as a function of unsaturated hydrocarbon flow rate using DEMS as a primary precursor and ethylene as a secondary precursor. Dielectric constant doesn't decrease but slightly increases with increasing ethylene flow rate and film stress almost doesn't change. This result was unexpected to us. Prior to experimentation, we believed that the unsaturated bonds in the hydrocarbon compounds would aid crosslinking of the primary organosilicon precursor and we would obtain results similar to using an unsaturated organosilicon precursor. As a result of our experimentation, we now believe unsaturated hydrocarbons are less effective at crosslinking the primary organosilicon precursor and/or may even polymerize during the PECVD process.
6. We also found in our work that primary CDO precursor + carbon-carbon triple bond containing organosilicon secondary CDO precursor are critical in obtaining low dielectric constant compared with using a carbon-carbon triple bond containing organosilicon CDO precursor only.
7. Attached in Appendix B is a comparison of a process using TMCTS as a primary precursor and ETMS as a secondary precursor with a process using ETMS alone. In process A, we used ETMS alone. Table 1 shows the optimized conditions used to obtain the film. The as-deposited film had a dielectric constant of 2.64 (measured using our standard k measurement). The as-deposited film had a dielectric constant

of 2.64 using the same standard k measurement. Process B shows TMCTS and ETMS. Here, the as-deposited film we were able to obtain had a dielectric constant of 2.54. These results were unexpected as at that time such a low dielectric constant (using a comparable measurement of dielectric constant) had not been achievable. Without this data, I believe that most researchers would not have expected that the TMCTS + ETMS would result in a significant reduction in the dielectric constant that we showed. The results in Table 1 are representative of data from other experiments in that using a primary organosilicon CDO precursor with a secondary $C\equiv C$ -containing organosilicon CDO precursor produces lower k films than $C\equiv C$ -containing organosilicon CDO precursor alone using comparable measurements of dielectric constant.

8. I have also reviewed the Rhee reference and believe that the differences in dielectric constant shown in Examples 1-9 of Rhee and what we found in depositions of similar films (e.g., in Figure 2 of Appendix A and Process A in Table 1 of Appendix B) are solely due to differences in conducting the dielectric constant measurement. We used an industry standard procedure for measuring the dielectric constant. I believe that if we measured dielectric constant of the films following the examples of the films in Rhee by this method, the results would be consistent with the data in the Appendices. Similarly, if we were to measure the dielectric constant of Process B in Table 1 with the same method of dielectric constant Rhee used, I believe we would obtain a dielectric constant below that Rhee found for ETMS alone, consistent with the results shown in Table 1.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true. I further declare that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both (under Section 1001 of Title 18 of the United States Code), and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.


Qingguo Wu

9/10/2007
Date

Appendix A

Figure 1. Dielectric constant and stress as a function of unsaturated CDO precursor flow rate. Primary CDO precursor is DEMS and secondary CDO precursor is TMSA (ETMS).

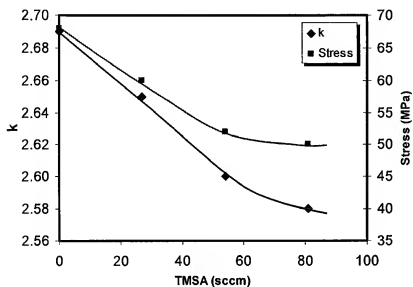
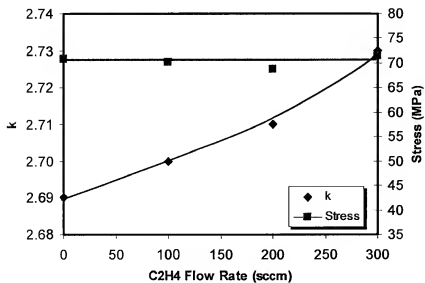


Figure 2. Dielectric constant and stress as a function of unsaturated hydrocarbon compound flow rate. Primary CDO precursor is DEMS and secondary precursor is ethylene (C₂H₄).



Appendix B

Table 1: Comparison of Primary Organosilicon Precursor + Secondary C≡C-containing Organosilicon Precursor With Single C≡C-containing Organosilicon Precursor

Process	Primary CDO precursor (TMCTS) flow rate	Secondary C-C Triple Bond Containing CDO Precursor (ETMS) flow rate	CO ₂ and O ₂ flowrates	Pressure	Total RF Power	Dielectric constant
Process A C≡C containing CDO Precursor Alone (ETMS)	0	1.5 ccm	5000 sccm	7 Torr	1000 W	2.64
Process B Primary CDO Precursor + C≡C containing Secondary CDO Precursor (TMCTS + ETMS)	1 ccm	0.4 ccm	5500 sccm	11.5 Torr	800 W	2.54